Measurement of hydroxyl radicals in plasma pencil by laser induced fluorescence

J. Voráč, P. Dvořák, V. Procházka

Dep. of Physical Electronics, Faculty of Science, Masaryk University, Brno, Czech Republic

Laser induced fluorescence was used for measurement of concentration of hydroxyl (OH) radicals in the plasma pencil, which is a radiofrequency plasma jet operated in argon at atmospheric pressure. The problematic of the rotational energy transfer, spectral overlap of the laser line and hydroxyl absorption line and saturation effects were treated. The method was calibrated by Rayleigh scattering on the ambient air. The concentration of hydroxyl radicals in the effluent of the plasma pencil was found to be in the order of $10^{20}\,\mathrm{m}^{-3}$. Dependence of hydroxyl concentration on argon flow rate and RF power delivered to the plasma were measured. Thy hydroxyl concentration was maximum at conditions, when the measurement point was close to the tip of the visible active discharge.

1. Introduction

The hydroxyl (OH) radical is frequently generated in electric discharges ignited in gases containing water vapour or organic compounds and oxygen. Since this radical belongs to the strongest oxidative species, it significantly influences plasma chemistry and surface treatment. Moreover, hydroxyl radicals are a source of intense UV radiation. Consequently, knowledge of hydroxyl concentration in discharges is desirable.

From the practical point of view, discharges ignited at atmospheric pressure are advantageous for surface treatment. In this work, the hydroxyl concentration was measured in the so called plasma pencil. Plasma pencil is a monopole RF plasma jet ignited in argon inside a quartz capillary [1–4]. Argon at atmospheric pressure is blown out from the capillary and mixes with ambient air. If the values of argon flow rate and RF power are sufficient, the active plasma penetrates outside the quartz capillary and can be used e.g. for surface treatment.

The hydroxyl concentration was measured by laser induced fluorescence (LIF), which is a sensitive method and enables spatially resolved concentration measurements. Only a limited number of quantitative hydroxyl concentration measurements realized by LIF in atmospheric discharges has been published. In flames, a careful work was made by Crosley at al. [5]. Recently, the hydroxyl concentration in argon plasma jets [6, 7], helium plasma jet [8] and dielectric barrier discharge [9] was measured.
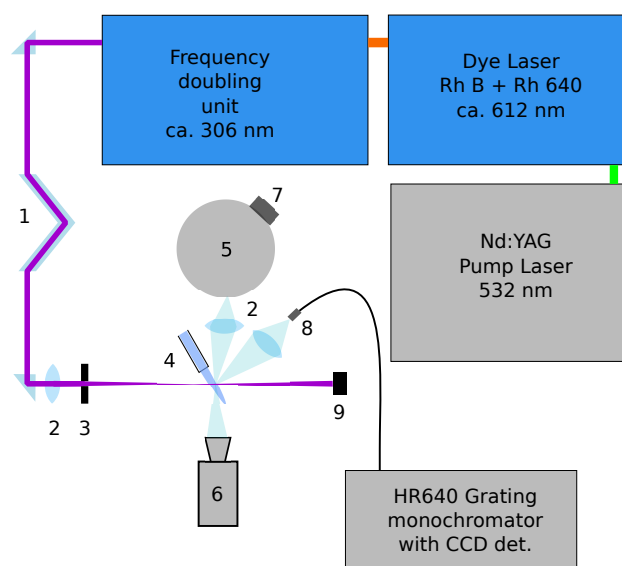

Fig. 1: Diagnostic setup. 1 – Fresnel rhomb, 2 – quartz lens, 3 – iris diaphragm, 4 – plasma pencil, 5 – monochromator, 6 – ICCD camera, 7 – photomultiplier, 8 – optical fiber, 9 – laser energy meter

2. Experimental

A pulsed Nd:YAG laser (Quanta-Ray PRO-270-30) was used to pump a tunable dye laser (Sirah PRSC-D- 24-EG) with a frequency doubling unit to produce radiation with wavelength around 306.5 nm. The spectral line-width of the system is 0.4 pm. The output beam is horizontally polarised, which is disadvantageous for the Rayleigh-scattering measurement, which we used for the calibration. Therefore, a Fresnel rhomb was used to turn the laser polarization to vertical. The fluorescence was measured by an ICCD

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14. ABSTRACT
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camera. The fluorescence signal was significantly stronger than the background radiation. Therefore, background subtraction was fully sufficient and it was not necessary to use a wavelength filter. In parallel, the fluorescence was measured by a photo-multiplier tube behind a high-transition prism monochromator. Further, the spontaneous emission of the OH radicals was recorded with a CCD detector behind a high-resolution grating monochromator (HR-640) to extract the rotational temperature.

The hydroxyl concentration was measured in the effluent of the plasma pencil, 2 mm from the end of the quartz capillary.

3. Laser induced fluorescence

The laser wavelength was tuned to the line R$_1$(4) of the X$\,^2\Pi(v'' = 0) \rightarrow$ A$\,^2\Sigma^+(v' = 0)$ vibronic band. By this excitation wavelength, the lowest vibrational level of the A$\,^2\Sigma^+$ state was excited and the vibrational transfer in the excited state was avoided. The disadvantage of this excitation schema is the fact, that the wavelength of the scattered laser coincides with the wavelength of the measured fluorescence. However, the life time of the excited state in argon environment was much higher than the laser pulse duration. Therefore, the collection of the fluorescence radiation was started after the end of the laser pulse in order to avoid a distortion of the measured signal by the scattered laser light. The portion of the lost fluorescence signal was calculated and added to the measured signal. Quenching rate of the excited state was determined directly from time-resolved fluorescent measurements without necessity of knowledge of the gas composition in the measurement point.

The rotational energy transfer in the excited state was found to be very fast. Therefore, the rotational distribution was assumed to be thermalized. Since the fluorescence radiation of the whole vibronic band was detected, the effective Einstein coefficient of radiative transitions from the excited state was determined as a weighted sum of all detected transitions from various rotational levels. Since the rotational distribution in the ground vibronic state can be assumed to be thermalized as well, the total amount of hydroxyl radicals in the ground vibronic state can be calculated from the measured concentration of the X$\,^2\Pi(v'' = 0)$, $J = 4$ state by means of measured rotational temperature.

Further, saturation effects were treated in the LIF measurement. Weak saturation influences not only the intensity of the measured signal, but it affects the apparent spectral overlap of the laser line and absorption line used for excitation as well.

Fluorescence measurements were calibrated by Rayleigh scattering on air at atmospheric pressure. This simple calibration method was enabled by the use of ICCD camera which enables to distinguish between the measured fluorescence/scattering signal and eventual scattering on surrounding objects. Details of the measurement and evaluation procedure can be found in [7].

4. Hydroxyl concentration

The hydroxyl concentration in plasma pencil was measured as a function of argon flow rate and RF power [7]. The maximum hydroxyl concentration was around 5×10^{20} m^{-3}. Its dependence on argon flow rate is shown in the fig. 2. The discharge can be easily operated in argon but its expansion into air is difficult. Consequently, the active discharge is short and is enclosed in the capillary at low argon flow rates, which results in low hydroxyl concentration in the measurement point outside the capillary. Increase of argon flow rate led to an elongation of the visible active discharge and increase of measured hydroxyl concentration. When the tip of the active discharge reached and surrounded the measurement point, the hydroxyl concentration reached its maximum. Further increase of argon flow rate led to a decrease of hydroxyl concentration, which can be explained by an elongation of the active discharge and a consequent decrease of spatial density of absorbed RF power.

A similar behaviour was found by measurement of the dependence of hydroxyl concentration on RF power. At low RF power, the active discharge was short and did not reach the end of the capillary. Therefore, the hydroxyl concentration in the effluent (outside the capillary) was small. Increase of RF power led to a strong increase of hydroxyl concentration up to the moment when the active discharge reached the measurement point. Further increase of RF power and active discharge length caused a slight decrease of hydroxyl concentration, as can be seen in the
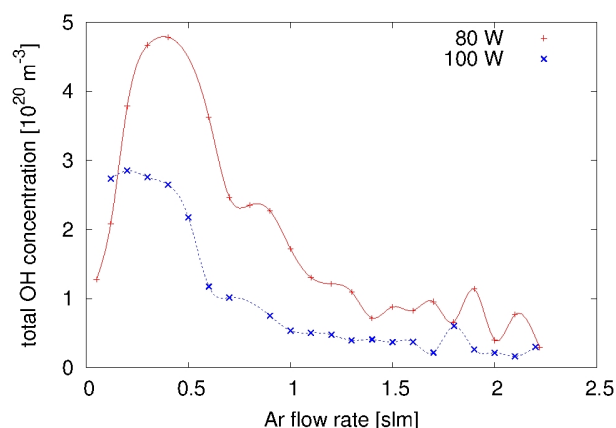
Fig. 2: Hydroxyl (OH) radical concentration in the effluent of the plasma pencil as a function of argon flow rate for two various values of the RF power delivered to the plasma.

fig. 2. Since the total RF power delivered to the discharge from the RF generator was not constant in this case, the hydroxyl concentration decrease can not be explained simply by the decrease of RF power density. We expect that the hydroxyl production rate is highest at the tip of the active discharge, where the electron concentration is low and the electric field (and electron energy) is expected to reach its maximum. However, this explanation should be tested by a spatially resolved LIF experiment.

Acknowledgement

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